

Approved For Release STAT
2009/08/17 :
CIA-RDP88-00904R000100100

declassified

Approved For Release
2009/08/17 :
CIA-RDP88-00904R000100100



**Third United Nations
International Conference
on the Peaceful Uses
of Atomic Energy**

A/CONF.28/P/345

USSR

May 1964

Original: RUSSIAN

Confidential until official release during Conference

**EXTRACTION-CHROMATOGRAPHIC ISOLATION
OF AMERICIUM AND CURIUM**

V.M. Vdovenko, A.S. Krivochatskij, M.P. Kovalskaja,
E.A. Smirnova, S.M. Kulikov, N.A. Aleksjeva,
L.M. Bjelov

The preparation of pure Am and Cm is necessary for studying the chemical and nuclear properties and for technical use of these elements. Transplutonium elements are produced by irradiation of Pu and U with high integrated neutron flux in nuclear reactors. While irradiating the considerable quantities, the feed material is dispersed in an inert filler which ensures the required heat removal; the small quantities may be irradiated without a filler. Magnesium metal is used as the filler. The dissolution of irradiated magnesium-ceramic blocks is attained by nitric acid treatment. The reprocessing of the solution thus obtained must provide the separation of actinides from macrocomponent, if any, the purification of Am-Cm from Pu, their separation from rare earths (fission products) and, finally, the separation of Am from Cm.

The first problem can be easily solved by extraction of Am, Cm and R.E.; plutonium is preliminary extracted as well. We have used phosphororganic compounds, tertiary amines and thenoyl trifluoroacetone (TTA) as the extractants for plutonium extraction from the solution with salting-out agent; TTA is used for extraction from saltless solution. The resulting concentrate of Am and Cm can be then reprocessed by means of extraction and chromatographic methods; it is most advisable to accomplish the preliminary purification with the help of di - (2-ethylhexyl)-phosphoric acid (D2EHPA) and

25 YEAR RE-REVIEW

tri-n-decylamine (TDA) from the concentrated solutions of lithium chloride; the complete purification is performed with chromatography by using hydrochloric acid and ammonium- α -hydroxyisobutyrate as the eluents.

I. Extraction of Am and Cm.

The solutions obtained as a result of the dissolution of irradiated samples are rather convenient, from standpoint of their composition, for the separation of Am and Cm from Pu.

Pu (IV) may be readily extracted with TTA (1,2,3) from nitric acid solutions. For plutonium extraction from irradiated materials containing Am, Cm and fission products we have used 0.2M TTA-benzene solution. The aqueous solution for the extraction was adjusted to acidity of 0.5 M; Pu was stabilized in tetravalent state by sodium nitrite. While extracting with TTA, kinetics is an important factor as the reaction rate of chelate formation is low and therefore has a great influence on the extraction. In order to determine the rate of Pu (IV) extraction, we have studied the effect of contact phase time on the value of its extraction in horizontal pulsed column. The capacity of the mixing section was equal to 135 ml. The use of such a column enables to choose the conditions under which interphase is changed slightly at different efficiencies. As a continuous phase, 0.2 M TTA-benzene solution was used. The aqueous solution containing Pu was passed through the column at the variable rate. For comparison, extraction kinetics was studied not only on 0.5 M nitric acid solution, but also on the solution containing salting-out agent.

The obtained data are shown in Figure 1.

The amount of the extracted plutonium depends greatly

on the phase contact time.

The rate constant of reaction was determined according to Goldschmidt's equation (4). The value of the constant "Ka" in the case of extraction from 0.5 M nitric acid was as high as $(0.33 \pm 0.03) \text{ min}^{-1}$. In the presence of magnesium nitrate the value of this constant was several times less: $K = (0.09 \pm 0.03) \text{ min}^{-1}$; this exhibits the great influence of salt concentration in solution on the extraction rate.

From the solutions which contain nitric acid and large amount of magnesium nitrate, plutonium is isolated by means of liquid extraction with such solutions of phosphororganic compounds as TBP and D2EHPA or with TOA and TDA in inert diluents.

The distribution coefficients of Pu (IV) and Cm for extractants cited above are summarized in Table I.

Table I
Distribution Coefficients of Pu and Cm

Composition of aqueous solution (M)		Composition of extractants	Distribu- tion coef- ficients of Pu(IV)	Distribu- tion coef- ficients of Cm
<u>Magnetic :Nitric nitrate :acid</u>				
2.5	1.33	5% TBP in decane	43	0.005
2.5	1.94	0.001M D2EHPA in decane	300	0.003
2.5	1.30	0.2M TDA in decane	130	0.002
2.5	3.00	0.2M TOA in benzene	27	-

The values of distribution coefficients indicate that all the extractants listed above can be used for plutonium extraction, providing the high degree of purification from Am and Cm. Transplutonium elements remain completely in aqueous solution.

The group separation of transplutonium elements and rare earths is considered to be a step in Am and Cm purification from mactocomponent, if present, and from many fission products. The extraction of these elements can be conducted both from pure solutions and from solutions containing salting-out agent. In the first case, chelating agents can be used as the extractants for isolation of actinides and lanthanides from solutions at low acidity (1, 5). In the second case, neutral phosphororganic compounds (6,7) are utilized as extractants; the content of excessive acid in the solution should be as low as possible to avoid the competition between the extractable metals

345

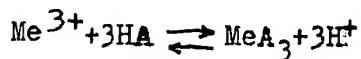
and the acid.

The published data on Am and Cm extraction with TTA contain no information concerning the ways of keeping the required value of pH in the solution and the influence of diluent on the extraction; this limits the applicability of extraction of transplutonium and rare earth elements with the help of TTA. We have studied the effect of diluent on the extraction of Am, Cm and R.E. (Ce, Eu, Tu, Tb, Lu) with 0.2M and 0.05M TTA solutions. The pH-value of solution was adjusted by addition of small quantities of nitric acid or ammonia.

The data obtained for extraction of Cm and Tb are represented in Figures 2 and 3.

In the range of investigated pH-values the extraction of elements from aqueous solutions increases on increasing pH of feed aqueous solution; at the further increase of pH, the hydrolysis of metals begins to affect the process.

The values of distribution coefficients are influenced by diluent. The higher values of the distribution coefficients are obtained by use of oxygen-containing diluents. In order to determine the composition of the compounds in organic phase, we have studied the dependence of distribution coefficient on hydrogen ion concentration in aqueous solution and on TTA concentration in organic phase. The obtained distribution coefficients are directly proportional to the third power of TTA concentration and inversely proportional to the third power of hydrogen ion concentration. Thus, the extraction can be expressed by the equation as follows:



To ascertain the reasons for higher extractability of the investigated elements while using oxygen-containing

345

diluents, the method of dilution was utilized. At the constant concentration of TTA in organic phase, the composition of this latter was changed with changing the ratio between the highly extracting oxygen-containing diluent and the poorly extracting diluent (benzene).

In Figure 4 the data are given which were obtained for the dependence of the distribution coefficients of terbium on the concentration of amyl acetate or dibutyl ether in TTA-benzene solutions at the constant concentration of TTA and hydrogen ions. The results produce a strong evidence for formation of solvate of $\text{Me}(\text{TTA})_3\text{S}$ in organic phase (S - molecule of oxygen-containing diluent). The formation of solvate is responsible for the higher extractability of transplutonium and rare earth elements while using the oxygen-containing diluents of TTA.

In the further investigation, some buffer solutions have been used to attain the certain stable values of pH. It is clear from the results obtained that, depending on the used buffer solution, the quantity of the extractable element may be more or less as compared with the quantity of the same element extracted from the solution without any buffer. For example, at pH=3.5 the equal volume of 0.2 M TTA in benzene extracts about 70% of Cm from acetate buffer and about 20% from citrate buffer; in the absence of buffer solution, 40% of curium can be extracted at the same value of pH. The information on Am and Cm extraction with 0.2M TTA-solutions from acetate buffer is given in Figure 5. The most favourable results were obtained for the extraction from acetate buffer with TTA solutions in amyl acetate.

Kinetics is also of great importance for Am and Cm extraction. The investigation of the rate of Cm extraction with TTA-solution in benzene was conducted in horizontal pulsed column under the above-mentioned conditions.

The data obtained are reported in Figure 6. The values of the rate constant for heterogenous reaction calculated in accordance with Goldschmidt's equation were found to be in the order of $(0.57 \pm 0.06) \text{min}^{-1}$ in both cases of extraction in the presence of magnesium nitrate and without it.

To extract americium and curium from the solution containing salting-out agent, the same extractants may be used as those for plutonium extraction. However, the concentration of extractant in the organic solution should be considerably higher.

The distribution coefficients of transplutonium elements are greatly influenced by nitric acid concentration in aqueous solution. The data on curium extraction with the extractants described above are represented in Table II.

These results have meant that transplutonium elements can be extracted from aqueous solution of magnesium nitrate provided the concentration of nitric acid is not high. The best results have been received for extraction by 40% -solution of TBP in decane. In all these cases the main impurities are rare earths and iron (if present in aqueous solution) which are extracted into organic phase under these conditions as well.

Table II
Dependence of distribution coefficients of curium on nitric acid concentration in aqueous solution containing 2.5 M magnesium nitrate.

Extractant	Distribution coefficient						
	T.B.P. M:I.I N:0.4 M:pH=0.3:pH=1.2:pH=2.3:pH=2.6						
40% TBP							
in decane	1.8	2.2	13	62	69	70	-
0.36M D2EHPA							
in decane	-	3.2	-	-	30	-	-
0.8 TDA in benzene	-	-	-	-	2.4	3.2	2.0
345			7				

2.Extraction separation of actinides and rare earths.

The concentrate of Am and Cm obtained as a result of extraction contains considerable quantities of fission rare earths which often exceed the content of Am and Cm. Because of high specific activity of rare earths and actinides, it is advisable to remove the bulk of fission products by means of extraction. In the literature some methods are described for separation of rare earths and actinides by use of extraction with amines and alkyl phosphoric acid from lithium chloride solutions (8, 9).

We have studied the group separation of transplutonium and rare earth elements by means of extraction from concentrated solutions of lithium chloride with the help of D2EHPA and TDA chloride in different diluents, depending on the composition of aqueous solution, the concentration of extractants and the diluent. In Table III the data are shown on the extraction of some trivalent elements with D2EHPA in different diluents from aqueous solutions of lithium chloride at various content of hydrochloric acid.

Table III

Dependence of isolation of actinides and lanthanides
on extraction conditions with 0.3 M D2EHPA.

Diluent	Concentration :		% of Extraction					
	: LiCl : (M)	HCl : (M)	: Am	: Cm		: Eu	: Tb	: Tm
				:	:			
Polyalkyl benzene	13.0	0.007	11.9					92.6
"	12.0	0.007	10.3					84.8
"	13.0	0.010		17.2		74.7		
"	12.0	0.010		9.6		73.5		
"	13.0	0.040		7.9	30.1		81.0	
"	12.0	0.040		5.1	19.8		76.0	
Octane	13.0	0.003	25.7					
"	13.0	0.068	13.9	16.3	43.1	64.5	68.4	83.7
Kerosene	13.0	0.003	21.8					
"	13.0	0.068	9.6	13.4	34.2	49.3	51.3	55.7
O-xylene	13.0	0.007	3.7	9.3	13.5	82.8	86.5	
"	12.0	0.007	3.5	9.0	12.4	69.1	84.5	
"	12.0	0.135	0.5	1.1	1.2	6.3	29.5	

It is clear that rare earths are chiefly extracted with D2EHPA from the solutions of lithium chloride; the extraction increases markedly with atomic numbers. Curium and americium are extracted to a small degree; for these reasons, it is possible to carry out the group separation of lanthanides and transplutonium elements by means of extraction from lithium chloride solutions. The D2EHPA-extraction is dependent on the concentration of lithium chloride and hydrochloric acid in aqueous solution. The distribution

coefficients of elements under review decrease with the increase of hydrochloric acid concentration in the solution.

The other investigated extractant is 20% TDA-chloride which was used for extraction from the solution containing 0.015 M hydrochloric acid and 1.5 M lithium chloride. The results obtained are shown in Table IV.

Table IV
Extraction of curium and europium with 20% TDA-solution in different diluents.

Diluent	% of curium extraction	% of europium extraction
n-octane	TDA-HCl does not dissolve	
Carbon tetrachloride	22.0	0.6
Benzene	65.6	11.4
Toluene	71.6	9.6
Xylene	91.0	21.6
Chloroform	0.01	0.01
Chloro-benzene	77.6	9.6
iso-amyl acetate	64.4	5.6
β, β' -Dichloroethyl ether	78.4	35.6
Nitro-benzene	71.4	21.0
Polyalkyl benzene	83.4	18.6
Dibutylcarbitol	55.8	4.8

All the investigated diluents have a great influence on amine extraction of Cm and Eu. As a whole, curium is extracted considerably better than europium, irrespective of the diluent employed.

Figure 7 and Table V show the effect of lithium chloride concentration on curium and europium extraction from aqueous solutions containing 0.015 M hydrochloric acid by means of 20% TDA-chloride solution in different diluents.

One can see in Figure 7 the strong dependence of curium extraction on lithium chloride concentration. The extraction of curium becomes appreciable only after lithium chloride concentration attains 9 M. In the studied range of concentrations, curium is extracted much better than europium; this means the possibility of separation by utilizing nearly all diluents cited above.

It is shown in Table V that the highest distribution coefficient (α) of curium for TDA-extraction has been observed in that system where amine is dissolved in xylene; the separation factor (D) for Cm and Eu have also the highest values in this system. As the concentration of lithium chloride in aqueous solution decreases, the separation factors increase for all the diluents under consideration.

The experimental data concerning the dependence of TDA-extraction of Cm and Am on the acidity of aqueous solution containing lithium chloride have shown that the extraction of Cm and Eu decreases with increase of acid concentration irrespective of the diluents employed. In Table VI the data on the separation factors (D) are summarized depending on the concentration of TDA-chloride in xylene. According to these results, the higher concentration of the extractant decreases Cm-Eu separation factors (D).

345

Distribution coefficients of curium and europium for
the extraction with 20% TDA-solution from lithium
chloride solution

Table V

LiCl : (M)	Xylene	Polyalkyl benzene	Chloro-benzene	Toluene	Nitro-benzene										
	d_{Cm}	d_{Eu}	d_{Cm}	d_{Eu}	d_{Cm}	d_{Eu}	d_{Cm}	d_{Eu}	d_{Cm}	d_{Eu}					
13.0	10.0	0.30	33	5.0	0.20	25	3.4	0.10	34	2.5	0.10	25	2.5	0.30	8.3
12.6	5.3	0.090	59	3.8	0.13	29	2.3	0.05	46	1.7	0.050	34	2.2	0.13	17
12.2	3.1	0.050	62	2.6	0.070	37	1.6	0.03	53	1.2	0.030	40	2.0	0.070	28
11.8	1.9	0.020	95	1.8	0.030	60	1.2	0.010	120	0.8	0.010	80	1.7	0.040	42
11.2	1.0	0.004	250	1.3	0.014	93	0.65	0.008	81	0.6	0.008	75	1.5	0.020	60
11.0	-	-	-	0.9	0.006	150	0.30	0.004	75	0.37	0.004	92	1.0	0.016	62

12

Separation factors of Cm and Eu depending on TDA-chloride concentration for the extraction from aqueous solution containing 13.4 M LiCl and 0.015 M HCl.

Concentration of TDA-chloride in vol.%	D
10	40
15	21
20	12
30	5

Thus, the combination of the extraction with D2EHPA and TDA has made it possible to obtain the satisfactory results in separation of Am and Cm, on the one hand, and rare earths, on the other.

3. Purification of Am and Cm by chromatographic method

The concentrates of transuranium elements obtained as a result of extraction processes contain still the considerable quantities of fission products and other impurities. The predominant impurities in Am-Cm fraction are lanthanides. The chromatographic methods of purification permit to prepare transuranium elements to higher degree of purity.

The separation of those elements which have many similar chemical properties is readily achieved by means of hydrochloric acid elution from cation-exchange resins (10, 11). The practical use of this method proves effective

while varying the concentration of hydrochloric acid which we used in our work. The change in hydrochloric acid concentration enables to prepare actinides to high degree of purification from lanthanides and residual macroimpurities (iron, magnesium, etc.). For separation purposes, the KU-2 resin was used which has a particle size about 0.2-0.4 cm/min. according to sedimentation. The separations were completed at room temperature in columns 80 mm in height and 3 mm in diameter. The results obtained indicate (see Fig.8) that the most favourable order of changing the eluent concentration was as follows (in the presence of lanthanides, actinides and macroimpurities such as iron, magnesium, etc.): first, 2-3M hydrochloric acid is sent; the macroimpurities are easily eluted by it, while the actinide and lanthanide elements remain on the resin; then the elution is conducted with 12-13 M hydrochloric acid for the rapid removal of actinides; at the same time, lanthanides are again left on the resin. At last, 6M hydrochloric acid is passed through the column to elute the lanthanide elements. In the absence of macroimpurities of iron and magnesium, the separation of Pu, Am and Cm from lanthanides is easily performed under the same conditions by means of 12 - 13 M hydrochloric acid, whereas lanthanides are eluted with 6 M hydrochloric acid.

As is evident from Figure 9, Pu, Am and Cm being separated from rare earths are practically eluted in the same peak; the influence of lanthanum (which is also often used as the carrier for transplutonium elements) on the group separation of actinides and lanthanides is seen from the chromatograms reproduced in Figure 10. It is noticeable that the poor separation of transplutonium and rare earth elements occurs at 10% load of resin capacity; on the further increase of lanthanum content, the separation

of rare earths and actinides does not practically occur. It is evident from the results obtained that the elution with hydrochloric acid of variable concentration allows to obtain in the same peak the Pu, Am and Cm fraction free from rare earths. Thus, the decontamination from many other fission elements and macroimpurities is attained in the course of these operations.

The preparation of individual transuranium elements with the help of complexing agents on the cation-exchange resin is believed to be the most preferable method which makes it possible to produce the transuranium elements in higher purity.

As reported by many investigators (12-15), ammonium- α -oxyisobutyrate is considered the best organic complexing agent. We have used this method for Am-Cm separation. It has allowed to perform the simultaneous decontamination from plutonium which is accumulated as a result of curium decay. While separating, the plutonium peak precedes the curium peak and, in practice, coincides with californium peak.

Figure 11 shows the results for separation of Pu, Am and Cm from each other on the KU-2 resin the particle size of which is of the order of 0.1 - 0.2 cm/min. at 85 - 90°C according to sedimentation.

The data on alpha-spectrometry and radiochemical analysis have shown that the impurities of alpha-emitters in peak fractions of separate elements do not exceed 10^{-2} - 10^{-3} % of alpha-activity.

References:

1. George H. Morrison, Henry Freiser. Solvent Extraction in Analytical Chemistry, New York, Wiley; London, Chapman and Hall (1957).
2. Moore F.L., Hudgens J.E., Anal. Chem., 29, (1957) 1767.
3. Gunningham J.G., Miles G.L., J. Inorg. Nucl. Chem., 3 (1956) 54.
4. Goldschmidt H., Messerschmidt A., Z. Phys. Chem., 31 (1899) 235.
5. Niese S., Beer M., Nauman D., Kopsel R., Extraktive Ausarbeitung bestrahlter Kernbrennstoffe Berl. 1960
6. Jakovlev G.N., Kosjakov V.N., Report № 2127 Proceedings of the 2nd Intern. Conf. on Peaceful Uses of At. En., Geneva (1958).
7. Zemlianukhin V.I., Savoskina G.P., Journal "Radiokhimija" (USSR), 3 (1961) 411.
8. Baybarz R.D., Leuze R.E., Nucl. Sci. Eng., 11 (1961) 90.
9. Moore F.L. Anal. Chem., 5 (1961) 748.
10. Katz J.J., Seaborg G.Th., The chemistry of the actinide elements. London, New York (1957).
11. Diamond R.M., Street K., Seaborg G.T., J. Am. Chem. Soc., 76 (1954) 1461.
12. Choppin G.R., Harvey B.G., Thompson S.G., J. Inorg. Nucl. Chem., 2 (1956) 66.
13. Milsted J., Beadle A.B., J. Inorg. Nucl. Chem., 4 (1957) 248.

14. Smith H., Hoffman B., J. Inorg. Nucl. Chem.,
3 (1956) 243.

15. Choppin G.R., Silva R.J., J. Inorg. Nucl. Chem.,
3 (1956) 453.

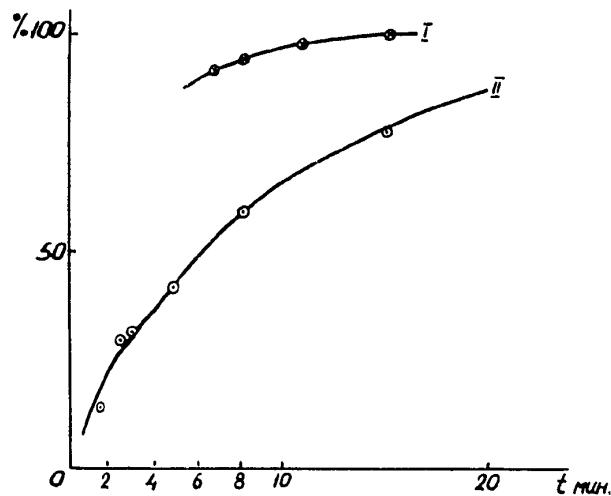


Fig. 1

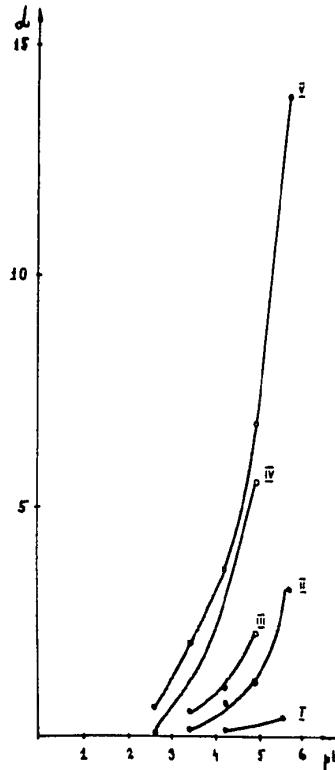


Fig. 2

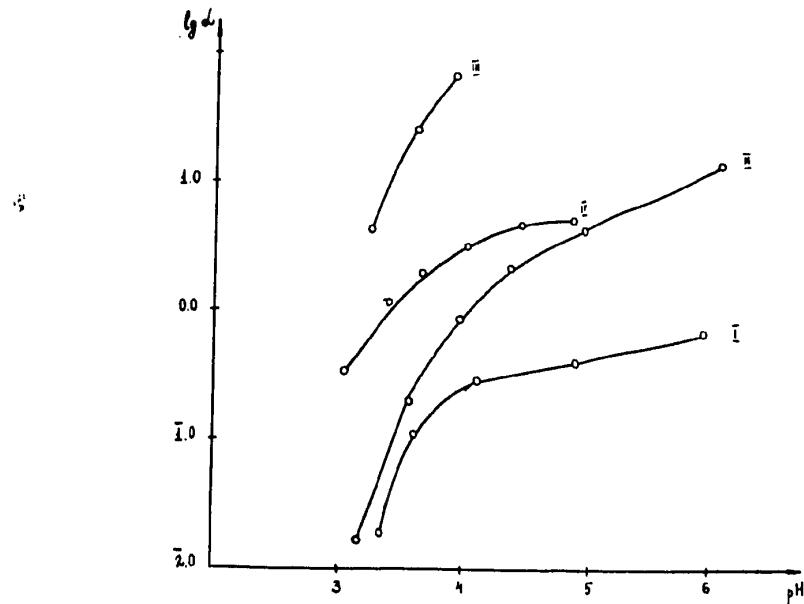


Fig. 3

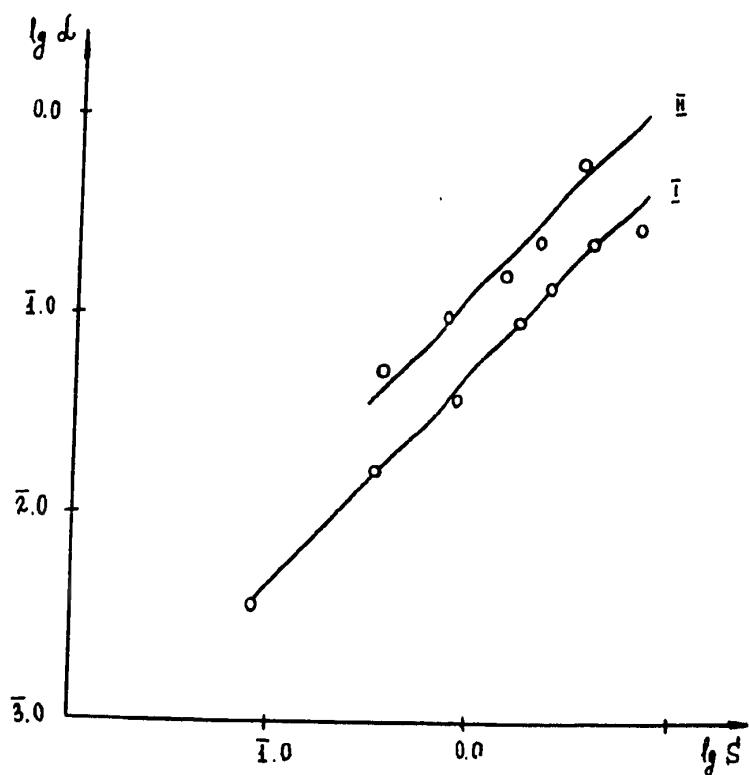


Fig. 4
345

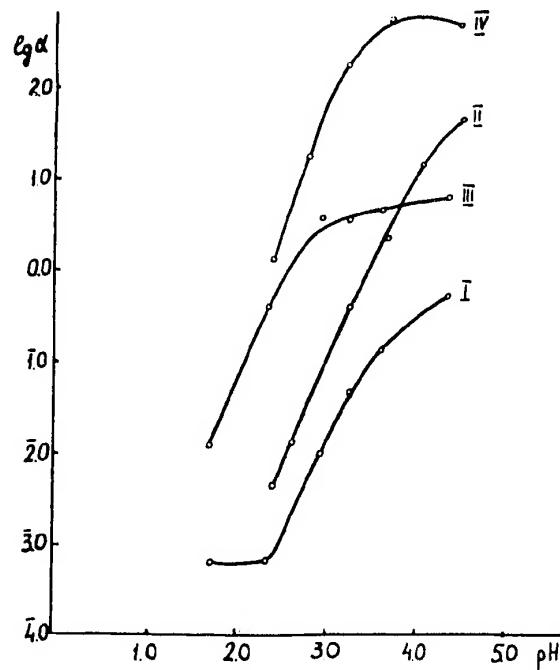


Fig. 5

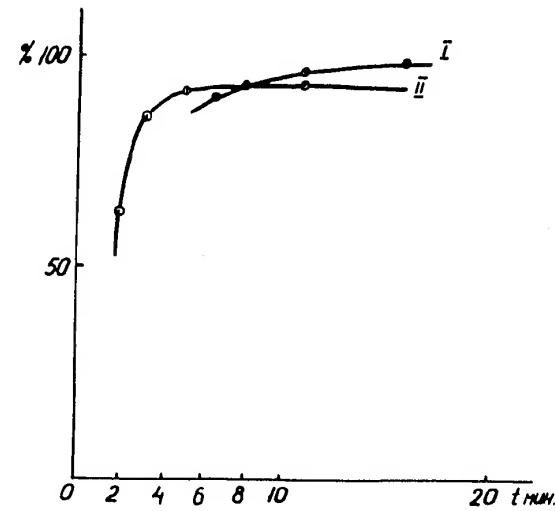


Fig. 6

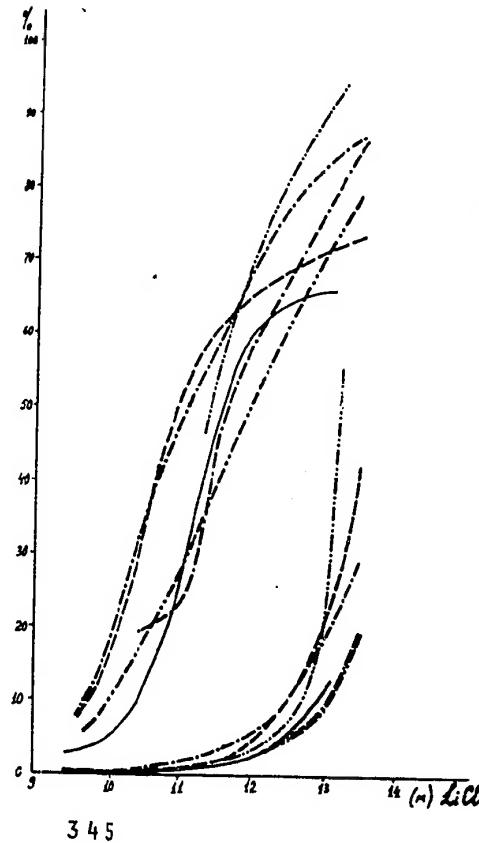


Fig. 7

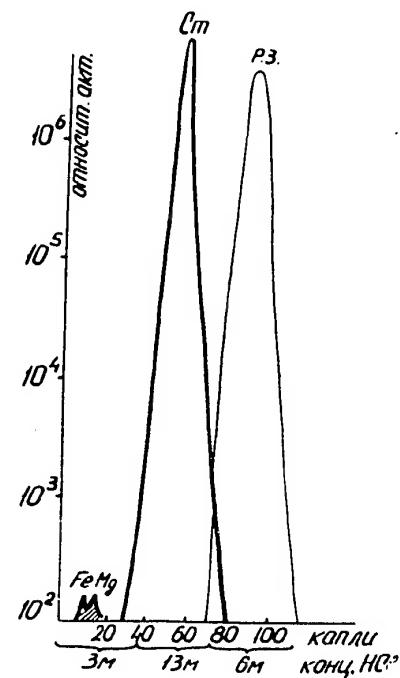


Fig. 8

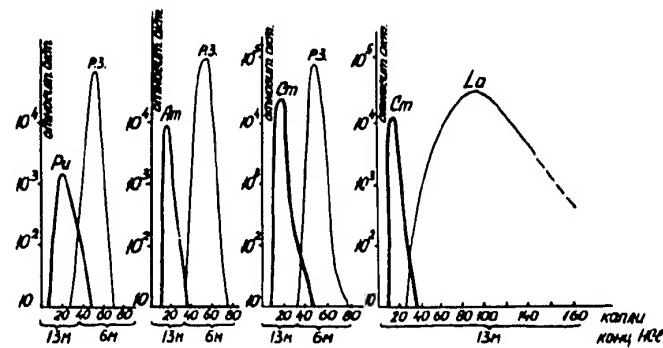


Fig. 9

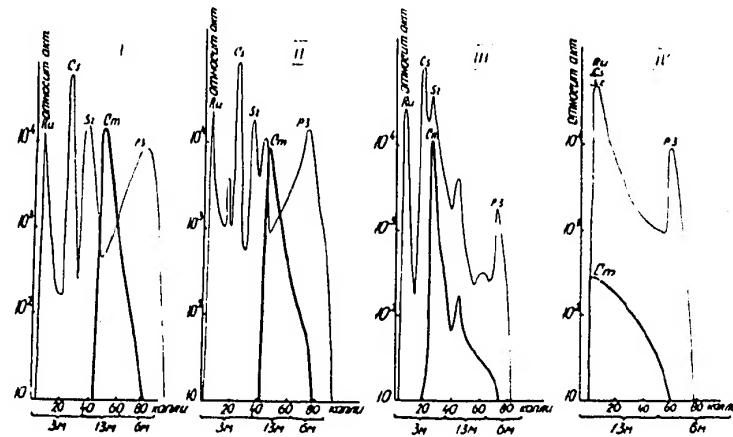
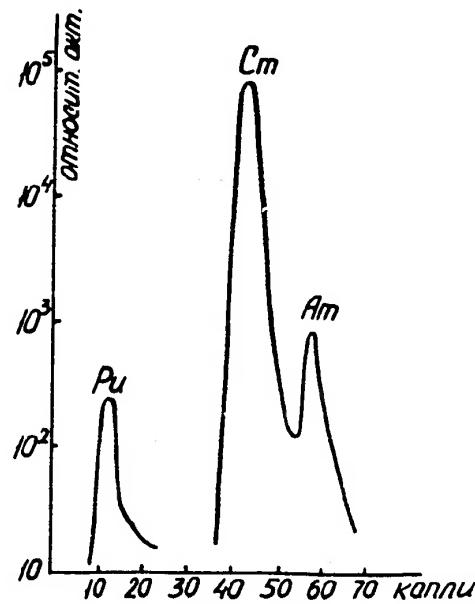


Fig. 10



345

Fig. 11

List of Figures

Fig.1. Dependence of Pu (IV) extraction with 0.2M TTA-benzene solution on phase contact time.

I - 0.5M nitric acid

II - 0.5M nitric acid + 3.5M magnesium nitrate

Fig. 2. Dependence of distribution coefficient of curium (α) on pH for extraction with 0.2M TTA solution in the following diluents:

I - choloroform; II - toluene; III - benzene;

IV - dibutyl ether; V - amyl acetate

Fig. 3. Dependence of distribution coefficient of terbium (α) on pH for extraction with 0.05M TTA solution in the following diluents:

I - benzene (the concentration of terbium nitrate - 10^{-4} M); II - benzene (the concentration of terbium nitrate - 10^{-5} M); III - amyl acetate; IV - dibutyl ether (the concentration of terbium nitrate - 10^{-4} M).

Fig. 4. Dependence of distribution coefficient of terbium (α) on the concentration of oxygen-containing diluents (S) as follows:

I - amyl acetate (0.1M TTA-benzene solution, pH=2.4, the concentration of terbium nitrate - 10^{-5} M);

II - dibutyl ether (0.15 M TTA-benzene solution, pH= 2.75; the concentration of terbium nitrate - 10^{-5} M).

Fig. 5. Dependence of distribution coefficient of americium (α) on pH-values for the extraction as follows:

I - 0.2M TTA-benzene solution;

II - 0.2M TTA-benzene solution from acetate buffer;

III - 0.2 M TTA solution in amyl acetate;

IV - 0.2M TTA solution in amyl acetate from acetate buffer.

Fig.6. Dependence of curium extraction with 0.2M TTA-benzene solution on phase contact time: I - acetate buffer; pH= 3.8; II - acetate buffer + magnesium nitrate; pH = 3.3.

Fig. 7. Dependence of curium and europium extraction with 20% solution of TDA-chloride in different diluents on the concentration of lithium chloride.

I - VI - curium extraction; VII - XII - europium extraction; I, VII - xylene; II, VIII - polyalkyl benzene; III, IX - toluene; IV, X - chloro-benzene; V, XI - nitro-benzene; VI, XII - benzene.

Fig.8. Chromatogram of purification of transuranium elements from macroimpurities of iron, magnesium and from microimpurities of rare earths for the elution with hydrochloric acid of variable concentration.

Conditions: height of column - 80 mm, diameter - 3 mm; KU - 2 resin, particle size - 0.2 - 0.4 cm/min. according to sedimentation; temperature 18°C.

Fig. 9. Chromatograms of Pu, Am and Cm separation from rare earths and lanthanum for the elution with hydrochloric acid of variable concentration. The conditions are the same as seen in Fig.8.

Fig.10. Chromatographic separation of transuranium elements and rare earths in the presence of macroquantities of lanthanum chloride. The conditions, see in Fig. 8, 9. In experiments I, II, III, IV, the load of column is equal to 0%, 1%, 10% and 100% of its capacity, respectively.

Fig. 11. Chromatogram of Am, Cm and Pu separation by use of 0.3M ammonium α -hydroxyisobutyrate.

Conditions: height of column - 70 mm, diameter -2.5 mm; KU-2 resin, particle size 0.1-0.2 cm/min. according to sedimentation; temperature 85-90°C; rate of elution- 100-110 sec per drop.